Shortcuts for understanding rovibronic spectroscopy of ultracold alkali metal diatomic molecules

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INVITED ARTICLE

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The high-resolution rovibronic spectroscopies of cold and ultracold molecules (e.g. supersonic molecular beam excitation spectra (MB), photoassociation spectra of ultracold atoms (PA), resonance-enhanced multiphoton ionization spectra (REMPI), stimulated Raman transfer (SRT) spectra) are of major current interest. This manuscript summarizes the significant level of understanding of these various spectroscopies, enabled by using simple graphical and semiclassical ideas and shortcuts. Physical realizations of these spectroscopies will be illustrated using the alkali metal diatomic molecules, both homonuclear (e.g. Rb2) and heteronuclear (e.g. KRb).

Keywords: spectroscopy; ultracold molecules; molecular beams; photoassociation; diatomic molecules; alkali metals

1. Introduction

1.1. The Born–Oppenheimer and Franck–Condon approximations

The understanding of both the rovibronic spectroscopy of diatomic molecules and the elastic scattering of two colliding atoms is based on the concept of the separation of slow nuclear motion and fast electronic motion in an atom or molecule. This gives rise to the Born–Oppenheimer approximation, whereby a potential energy curve (PEC) can be used to accurately describe the motion of the two nuclei within a diatomic molecule (as elaborated in Section 2), and the Franck–Condon approximation, whereby rovibronic radiative transitions between electronic states can be accurately described using the PECs and the electronic dipole matrix element between the initial and final rovibronic states (as elaborated in Section 3). In particular, these transitions, between initial and final rovibronic levels, indicated by horizontal lines between classical turning points of vibrational motion, and with instantaneous electronic transitions between PECs, represented by vertical lines, can readily be used graphically to determine the limits of strong transition probabilities and of semiclassical interference between different branches of the Mulliken Difference Potential (MDP). These considerations for ultracold alkali metal diatomic molecules in particular are then elaborated in Section 4.

A full treatment of the Born-Oppenheimer approximation is beyond the scope of this article. In addition to that fixed nucleus approximation, there are additional terms in the full diatomic Hamiltonian which slightly change the PEC (to the ‘adiabatic PEC’) and also couple a given adiabatic PEC with other adiabatic PECs, especially the electrostatic nonadiabatic terms, the spin-orbit terms, and the other terms related to the coupling of other angular momenta [1]. In what follows we will take PEC to mean adiabatic PEC unless otherwise specified. Often the coupling between the two PECs is very weak and almost completely negligible, especially for unperturbed ground states. In other cases the coupling can be quite strong, e.g. where two PECs avoid crossing each other. A classic example is the avoided crossing of the ground $X^1\Sigma^+$ and the first excited $A^1\Sigma^+$ states of LiH, shown in Figure 171 of [2] and discussed in [3]. In much of what follows, only an individual PEC and transitions to other individual PECs are considered without concern for coupling with two or more other perturbing PECs. In such cases, numerical solution of the radial Schrödinger equation for nuclear motion for such states is straightforward using well documented programs such as LEVEL [4]. In some cases, however, the coupling is essential to the process considered, e.g. to electronic predissociation of a rovibrational state in one PEC to a continuum state of a second PEC as discussed in Section 2.2 and to stimulated Raman transfer (SRT) to a singlet state through a coupled state of mixed singlet–triplet character from an initial triplet state as discussed in Section 4.6.

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Likewise, the treatment of the radial rovibrational part of the rovibronic wavefunction may be simple for a simple PEC with a single minimum, more complex for a more complex PEC with multiple extrema, and still more complex for mixed states involving two or more coupled PECs. Roughly speaking, these radial wavefunctions for the two PECs correlated to the lowest energy asymptote of two ground state alkali metal atoms are simple and uncoupled, while the radial wavefunctions for PECs correlated to the next set of asymptotes (with excitation of one of the two alkali metal atoms to the lowest 2P\textsubscript{J} states) are in general more complex, with more extrema and a variety of important couplings to other PECs. The higher asymptotes can be even more complex, but are only briefly discussed here.

The calculation of radiative transition probabilities (RTPs) (stimulated and spontaneous emission and (stimulated) absorption) between two states represented by two rovibronic wavefunctions in the simplest case of two unperturbed PECs (labeled e\textsuperscript{+} (upper) and e\textsuperscript{−} (lower)) involves an integration of the electronic wavefunctions over electronic coordinates to obtain an electronic dipole transition moment (EDTM) d\textsubscript{e-e}(R) and electronic selection rules, an integration of rotational angular wavefunctions over rotational angular coordinates to obtain rotational selection rules, and finally a radial integration over d\textsubscript{e-e}(R) between the upper |e\textsuperscript{+}, v\textsuperscript{+}, J\textsuperscript{+}\rangle and lower |e\textsuperscript{−}, v\textsuperscript{−}, J\textsuperscript{−}\rangle radial wavefunctions (e.g. from LEVEL [4]) to obtain the RTPs, which are all proportional to the square of the matrix element \langle e\textsuperscript{+}, v\textsuperscript{+}, J\textsuperscript{+}|d\textsubscript{e-e}(R)|e\textsuperscript{−}, v\textsuperscript{−}, J\textsuperscript{−}\rangle\textsuperscript{2}. The relative magnitudes of such squared radial matrix elements are often estimated using d = 1, independent of R, in which case they are called the Franck–Condon factors (FCFs). For localized levels, such as zero-point levels, this approximation usually works well, but it can have a large error for levels with a large separation of inner and outer turning points. For either the full matrix elements or the approximate FCFs, the regions of the inner and outer turning points often give the most important contributions to RTPs, with the intermediate region showing oscillatory behavior with local contributions of both signs. The wavelengths of these oscillatory behaviors are directly related to the local momenta of the moving nuclei in the two PECs, so there is an opportunity for a strong transition when the local momenta match. However, the relative phase of the two oscillations then determines whether the transition is strong or weak. The Mulliken Difference Potential (MDP) discussed in Section 2.3 provides a simple way of estimated the opportunity for significant RTPs between two PECs between the appropriate turning points for classical motion of the nuclei. It is also worth noting that for levels near dissociation, such as are frequently formed by ultracold photoassociation (PA), the region of the outer classical turning point at long range becomes much more important than the region of the inner turning point.

1.2. Relation to the Herschbach Group

A highlight of the first author’s graduate career in the Herschbach group (1964–68) was an extensive and elegant set of notes by Professor Dudley Herschbach summarizing the quantum mechanical and semiclassical bases of the elastic scattering of two atoms. While it took considerable discussion and study to appreciate the subtleties, it was especially helpful because of the physical insight it provided into various scattering phenomena, e.g. glory oscillations, rainbows, and orbiting resonances.

This graduate career focused on the scattering of H atoms from rare gases, H\textsubscript{2}, and Hg. The deepest PEC among those interacting species was H + Hg; for this reason it was predicted to be the best among those systems in which to try to observe glory oscillations, which had been observed in other systems, and orbiting resonances, which had not been observed by scattering. However, orbiting resonances had previously been observed in a different way; they corresponded to rotational predissociation of diatomic molecules, as had been pointed out for HgH in [5]. In short, they corresponded to quasibound levels of the HgH molecule, which predissociate by tunneling through the barrier in the effective PEC. Fortunately a number of such rotationally predissociative HgH levels had been observed in [6,7].

Moreover, there were considerable additional spectroscopic data for the HgH molecule. These data allowed the construction of the PEC for H + Hg interactions in the ground \textsuperscript{1}Σ\textsuperscript{+} state using the semiclassical Rydberg–Klein–Rees (RKR) method to determine the turning points of classical motion [8]. This PEC allowed accurate calculation of the dependence of the elastic scattering cross-section on the relative kinetic energy or velocity of the atoms with no adjustable parameters and was in very good agreement with experimental results [9]. This was in contrast to previous atom-atom scattering analyses where the PEC was typically approximated by the Lennard–Jones 12-6 PEC or another simple analytic form with two or more parameters to fit.

The spin-offs of the above research on HgH included also generalizations of the semiclassical RKR method for non-zero rotation [10] and for properties which are functions of internuclear distance
R [11], and simple semiclassical expressions for the expectation values of the kinetic and potential energy of two nuclei in a diatomic molecule [12].

This work set one of us on a career at Iowa (1968–1993) and Connecticut (1993–present) where a major theme has been the exploration of PECs using principally laser spectroscopy techniques (including especially multiple resonance techniques and also bound → free (photodissociation) and free → bound (photoassociation) as well as the usual bound → bound techniques) and secondarily ab-initio or semiempirical theory (especially at long range). This career consistently emphasized the alkali metal diatomic molecules, since they have nearly the theoretical simplicity of H₂, but have visible and near infrared spectra much more amenable to study with tunable lasers than the ultraviolet and vacuum ultraviolet spectra of H₂. Since 1993, ultracold (T < 1 mK) spectroscopy, which is particularly sensitive to the long-range portion of PECs, has brought a powerful new technique for study of atom-atom PECs and thus has been emphasized. Here we present some of the insights and shortcuts, primarily graphical and semiclassical, we have achieved in this work.

2. Potential energy curves (PECs) and their quantum states

2.1. PECs

We know about PECs from a variety of sources: e.g. transport properties, scattering cross-sections, solid and liquid structure, atomic line broadening, rovibronic spectra, theoretical (ab initio and semiempirical) calculations, and calculation of long-range forces from the properties of separated atoms. For the species considered here, ultracold alkali atoms and diatomics, it is the last three sources which dominate our understanding, with the rovibronic spectra providing the precision and the short and long range theory providing the framework. Rovibronic spectra first provided the turning points of classical motion by the semiclassical Rydberg–Klein–Rees method, and later by specialized procedures to go beyond it, e.g. when there are more than two classical turning points or when semiclassical results are insufficiently accurate.

When one thinks about a PEC, one ordinarily envisages a simple form, like the Morse potential for chemically bound systems or a Lennard-Jones 12-6 potential for systems with a well due only to attractive van der Waals interactions. In the homonuclear alkali metal diatomics, the ground \( X^1\Sigma^+ \) state, corresponding to two electrons in binding \( \sigma_g \) molecular orbitals, is roughly Morse-like, while the lowest energy triplet state, \( a^3\Sigma^+_u \), corresponding to one electron in the binding \( \sigma_g \) orbital and one electron in the anti-binding \( \sigma_u \) orbital, is roughly Lennard–Jones-like.

The example of the \( X \) state of Rb₂ is shown in Figure 1, along with the \( a \) state; the corresponding states in KRb are shown in Figure 2. Here and in all figures, the energy is given in wavenumbers (cm⁻¹) and the internuclear distance \( R \) in Bohrs (\( a_0 \)). Both states in both molecules are ‘regular attractive’ PECs in the sense that they each have a single extremum between \( R = 0 \) (where the Coulombic repulsion between the nuclei sends the PEC to \( +\infty \)) and \( R = \infty \) (where the PEC approaches its asymptotic value, here the sum of the excitation energies of the two atoms, which we define as our zero for the ground asymptote). Here the extremum is the single minimum at the equilibrium internuclear distance, \( R_e \). The PECs of the \( X \) and \( a \) states are highly accurate, based on high resolution spectroscopic data [13,15].

With regard to the first two dipole-allowed excited states observed, the \( A^1\Sigma^+_u \) state (first seen in Na₂ and K₂ in 1874 [17,18]) is similarly regular, but the \( B^1\Pi_u \) state (also seen in [17]) is not; originally the \( B \) state was
thought to possess only an additional barrier extremum, but subsequently it was realized that when spin-orbit coupling was also considered, there was an additional minimum at long range [19,20]. The PECs for the states in Figure 1 correlating to the Rb₂ 5S + 5P₃ asymptotes are from \textit{ab initio} calculations [14], as are the corresponding states for KRb in Figure 2 correlating with the K(4P₃) + Rb(5S) and K(4S) + Rb(5P₃) asymptotes [16].

However, when one looks at large internuclear distances, a different kind of specifically ‘long range’ theory is appropriate, based on the properties of the separated atoms. In that limit, the two states correlating to the nS + nS limit, the \(X\) and the \(a\) states, are attractive with an identical leading long range \(C₆R^₆\) term. In the same long range limit, roughly half of the PECs are attractive and half are repulsive at the nS + nP₃ asymptotes, as shown in Figure 3 for Rb₂ and in Figure 4 for KRb. The leading long-range PEC terms go as \(\pm C₃R^⁻³\) for two identical atoms (e.g. Rb₂) and as \(\pm C₆R^⁻⁶\) for two different atoms (e.g. KRb), where the values of \(C₃\) and \(C₆\) take different values for the many different molecular electronic states.

A quick comment on notation for the homonuclear alkali metal diatomics is now appropriate: the lowest \(1\Sigma⁺_g\) state, the \(1\Sigma⁺_u\) state, is also known primarily as the \(X\) or simply the \(X\) state; the \(1\Sigma⁻_u\) state is known as the \(a\) state; the \(1\Pi_u\) state is known as the \(b\) state; the \(1\Sigma⁺_g\) state is known as the \(A\) state; and the \(1\Pi_u\) state is known as the \(B\) state. For heteronuclear diatomics, without \(g\) or \(u\) designations, the same labels are used except that the \(A\) state is the \(2\Sigma⁻\) state. In the literature and in this paper, both notations will be used.

A critical question is how the long range states in Figures 3 and 4 are connected to the short-range states in Figures 1 and 2; this is shown in Figures 5 and 6. Table 1 lists the 10 lowest-lying adiabatic (Born–Oppenheimer) states of Rb₂ in the short-range region near \(R_e\) and the number of their extrema as shown in
Figures 1, 3 and 5, while Table 2 lists the same (as shown in Figures 2, 4 and 6) for KRb. Note that for adiabatic states, no crossings of states with the same $\Omega$ and inversion symmetry occur within the Born–Oppenheimer approximation. Nevertheless, by convention, we show the diabatic PECs in Figures 1 and 2 for the $A$ and $b$ states (where the adiabatic component of the PECs of the 0$^+$ or 0$^-$ component of the $b$ state, for Rb$_2$ or KRb, respectively, should not in fact cross the adiabatic PEC of the $A$ state); similarly in Figure 2, we show the diabatic PECs (where the adiabatic PECs of the 0$^-$ and 1 components of the KRb 2 $^3\Sigma^+$ state

Table 1. The number of extrema in the adiabatic potential energy curves of Rb$_2$ correlating to low-lying asymptotes.

<table>
<thead>
<tr>
<th>Short range–Hund’s case (a)/(b)</th>
<th>Long range–Hund’s case (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$SS + SS$</td>
<td></td>
</tr>
<tr>
<td>$X^1\Sigma^+$</td>
<td>1</td>
</tr>
<tr>
<td>$a^3\Sigma^+_u$</td>
<td>1</td>
</tr>
<tr>
<td>$b^3\Pi_u$</td>
<td>1</td>
</tr>
<tr>
<td>$2^1\Sigma^+_g$</td>
<td>1</td>
</tr>
<tr>
<td>$1^3\Sigma^+_g$</td>
<td>1</td>
</tr>
<tr>
<td>$2^1\Sigma^+_e$</td>
<td>2</td>
</tr>
<tr>
<td>$B^1\Pi_u$</td>
<td>2</td>
</tr>
<tr>
<td>$1^1\Pi_g$</td>
<td>1</td>
</tr>
<tr>
<td>$1^3\Pi_g$</td>
<td>2</td>
</tr>
<tr>
<td>$2^3\Sigma^+_u$</td>
<td>0</td>
</tr>
<tr>
<td>$3\Sigma^+_u$</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. The number of extrema in adiabatic potential energy curves of KRb correlating to low-lying asymptotes.

<table>
<thead>
<tr>
<th>Short range–Hund’s case (a)/(b)</th>
<th>Long range–Hund’s case (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K(4S) + Rb(5S)$</td>
<td></td>
</tr>
<tr>
<td>$X^1\Sigma^+$</td>
<td>1</td>
</tr>
<tr>
<td>$a^3\Sigma^+$</td>
<td>1</td>
</tr>
<tr>
<td>$b^3\Pi$</td>
<td>1</td>
</tr>
<tr>
<td>$A^1\Sigma^+_e$</td>
<td>1</td>
</tr>
<tr>
<td>$2^1\Pi$</td>
<td>2</td>
</tr>
<tr>
<td>$B^1\Pi$</td>
<td>1</td>
</tr>
<tr>
<td>$K(4P) + Rb(5S)$</td>
<td></td>
</tr>
<tr>
<td>$3^1\Sigma^+$</td>
<td>1</td>
</tr>
<tr>
<td>$2^1\Pi$</td>
<td>2</td>
</tr>
<tr>
<td>$3^3\Sigma^+$</td>
<td>2</td>
</tr>
</tbody>
</table>

Figure 5. The connection at intermediate range of the short and long range potential energy curves of Rb$_2$, from [21].

Figure 6. The connection at intermediate range of the short and long range potential energy curves of KRb, from [25].
should not cross the adiabatic PECs of the 0− and 1 components of the adiabatic PEC of the b state); in Figure 6, the corresponding adiabatic states are shown, with the very small gap at the avoided crossing at \( \sim 12.2 \text{a}_0 \). Spin-orbit coupling is included on the right and thus individual triplet states (shown on the left at short distance as having degenerate \( \Omega \) components) split into two or four different \( \Omega \) components on the right at long range. Thus there is the relative simplicity of the 10 states on the left, with one ‘regular repulsive’ (no extremum) PEC (2 \( 3\Sigma^+_g \)), six ‘regular attractive’ (one extremum) PECs (\( X, a, b, A, 1 \ 3\Sigma^+_g, 1 \ 1\Pi_g \)), and three PECs with a second extremum (a barrier outside a potential well) (2 \( 1\Sigma^+_g, \ B \ 1\Pi_u, \ 1 \ 3\Pi_g \)). With the addition of spin-orbit coupling, there are 19 \( \Omega \) components on the right, with two ‘regular repulsive’ PECs (3\( 0\Sigma^+_g \) and 4\( 1\Pi_u \)) from \( 2 \ 3\Sigma^+_g \), ten ‘regular attractive’ PECs (1\( 0\Sigma^+_g \) from \( X \), 1\( 0\Pi_u \) and 1\( 1\Pi_g \) from \( a \), 1\( 0\Pi_g \) from \( b \), 2\( 1\Pi_u \) from \( A \), 1\( 0\Sigma^+_g \) and 1\( 1\Pi_g \) from \( 3 \ 3\Sigma^+_g \), and 2\( 1\Pi_u \) from 1\( 1\Pi_g \)), four two-extrema PECs (2\( 1\Pi_u \) from \( b \), 2\( 0\Pi_u \) from \( 3 \ 3\Sigma^+_g \), 3\( 1\Pi_u \) from 1\( 1\Sigma^+_g \)), two three-extrema PECs (2\( 0\Pi_u \) from 1\( 3\Pi_g \) and 3\( 1\Pi_g \) from \( B \), mentioned above), and one four-extrema PEC (3\( 0\Pi_g \)) from 1\( 3\Pi_g \), shown in Figure 5 for \( \text{Rb}_2 \), where the levels in the two corresponding potential wells have recently been observed [26].

Similar behaviour is seen for the states of KRb listed in Table 2. In particular, the two potential wells of the one four-extrema PEC (5\( 0\Pi_u \)) from the 2 \( 3\Pi_g \) state shown in Figure 6 (the analog of the 1 \( 3\Pi_g \) state in \( \text{Rb}_2 \)) are again observed [27]. Note that in both tables there are many ‘irregular’ PECs with \( \geq 1 \) extremum.

The other homonuclear and heteronuclear alkali metal diatomics are similar in their states and PECs. KRb is unique in that the atomic nP states and ionization potentials of K and Rb are the closest in energy among the heteronuclear molecules.

The numbering convention in the short-range region on the left is well known; it is based on the order of the adiabatic states at the equilibrium internuclear distance of the \( X \) state, \( R_e \). The numbering convention in the long-range region on the right is less well known. It is based on the order of energy of the atomic asymptotes first, with the numbering starting at \( 1 \) for the lowest asymptote. Then within a given spin-orbit asymptote, the numbering increases with increasing energy of the long range states. Thus in KRb, for example, in Figure 4, this last criterion is important for the numbering of the 3(1) and 4(1) states, and the 6(1) and 7(1) states. In asymptotes with a higher atomic degeneracy, the numbering will be more complex and also will involve calculations of the long-range interactions.

### 2.2. Quantum vibrational states

The quantum vibrational states of zero-extrema PECs are all continuum scattering states. Single extremum PECs show both continuum scattering states above dissociation and bound vibrational states below dissociation, usually with a linear decrease in spacing with \( v \) (as in a Morse potential) but with a nonlinear approach to dissociation due to the long range potential behavior discussed below. Two-extrema PECs normally include a well at short distance, with a barrier to dissociation at intermediate distance (e.g. \( \text{Rb}_2 \) [26]); thus the levels below dissociation are bound and often behave linearly with \( v \), while the levels above dissociation are quasibound, with a vast range of tunneling lifetimes from picoseconds to essentially bound in terms of lifetime for all practical purposes (e.g. up to \( 10^{29} \)s in [27]). Three-extrema PECs can be simply a double well potential with a barrier below dissociation in between (e.g. \( \text{Na}_2 \) [28]), where the levels near the top of the intermediate barrier can no longer be easily assigned to either well, and a barrier above dissociation in between (\( \text{Na}_2 \) [29]), where the levels in the two wells usually appear to be independent and not mutually perturbing. Four-extrema PECs correspond to a double well potential with a barrier in between the two wells and a barrier to dissociation from the outer well (e.g. \( \text{Rb}_2 \) [26] and KRb [27]). For these last two examples, no significant mixing between levels in the two separate wells was observed. Greater complexity is found in more highly excited states, but that will not be further pursued here.

It might also be noted that the outer well of the 3\( 0\Sigma^+_g \) component state of the \( \text{Rb}_2 \ 1 \ 3\Pi_g \) state [26] could, in addition to predissociation by tunneling [26], also in fact be electronically predissociated because of the avoided crossing with the 2\( 0\Pi_u \) state (at short range the 2 \( 1\Sigma^+_g \) state), producing a \( \text{Rb}(5\Pi_{3/2}) \) fragment atom. In the same way, the outer well of the 5\( 0\Sigma^+ \) component state of the KRb 2 \( 3\Pi_g \) state [27], in addition to predissociation by tunneling [27], could also in fact be electronically predissociated because of the avoided crossing with the 4\( 0\Sigma^+ \) state (at short range the 3 \( 1\Sigma^+ \) state) at \( \sim 19 \text{a}_0 \), producing a \( \text{K}(4\Pi_{3/2}) \) fragment atom. Interestingly, the 4\( 0\Sigma^+ \) state itself should be coupled to the 3\( 0\Sigma^+ \) state by their near crossing at \( \sim 13 \text{a}_0 \), possibly producing predissociation to the \( \text{Rb}(5\Pi_{3/2}) \) fragment. Finally, the 3\( 0\Pi^+ \) and 2\( 0\Pi^+ \) states have a short range crossing at \( \sim 9 \text{a}_0 \), but the crossing is expected to be quite diabatic, so predissociation to a \( \text{Rb}(5\Pi_{1/2}) \) fragment is not expected to be significant. Other couplings produce other predissociations for other \( \Omega \) component states, e.g. the predissociation of the KRb 1 \( 1\Pi \) state (4(1) at long range) to form \( \text{Rb}(5\Pi_{1/2}) \).
fragment atoms, possibly via several paths of intermediate states [25]. We are unaware of other examples where two or more competing predissociative channels have been found and understood in a single level. Theoretical calculations of these complex predissociations would be quite interesting.

The quantum rovibrational states are similar, but now it is the effective potential energy curve (EPEC)

$$U_j(R) = V(R) + \hbar^2 [J(J + 1) - f]/[8\pi^2\mu R^2]$$  \hspace{1cm} (1)

rather than the ordinary PEC, $V(R)$, which must be considered, where $f$ is dependent on the other angular momenta and Hund's case under consideration. For the case of no electronic spin or orbital angular momenta, $f = 0$. In general, $f$ is non-zero and off-diagonal coupling terms between levels of different PECs also arise in the diatomic Hamiltonian, as discussed in detail in Chapters 2 and 3 of [1]. In Hund's case (c), for example, $f$ is often taken to be $\Omega^2$.

Because of the $R^{-2}$ repulsion, there will ordinarily be quasibound levels above dissociation because of a new extremum in the EPEC when the long-range behavior is an attractive $-C_0 R^{-n}$ term, where $n > 2$. Moreover, there is always a maximum rotational quantum number $J$ for which the EPEC still shows one or more extrema, e.g. $J = 116$ for the $X$ state of $^6$Li$_2$ [30].

Because of the $R^{-2}$ behaviour, the number of extrema of EPECs can change further for PECs with unusual behavior. This was first observed in HgH [8], but has also been seen in alkali diatomics, e.g. the 4 $^1\Sigma_u^+$ 'shelf' state of Na$_2$, with a very flat PEC at intermediate $R$, where two additional extrema occur in the EPEC as the rotational quantum number $J$ increases [31,32].

In this paper, we will not give significant attention to actually solving for the radial (R-dependent rovibrational) wavefunction; rather we will concentrate on fairly localized levels, usually $r = 0$, and the inner and outer turning points of higher levels, $R_{in}$ and $R_{out}$, where the classical motion of a vibration turns around. Classical motion also slows near the maximum of a PEC or EPEC barrier, so there is a local enhancement of the wavefunction in those regions [33] and in the region of a shelf in the PEC [34].

Especially at long range (and thus near dissociation), the localization of the wavefunction in the region of the outer classical turning point becomes quite dramatic. For decades spectroscopists have sought observations of such levels (‘long-range molecules’), the behavior of which is determined primarily by long-range forces [35,36]. However, it is not easy to observe such species starting from the minimum of the $X$ ground state except by using multiple resonance spectroscopy [32,37]. Thus the development of the photoassociative spectroscopy of ultracold atoms has opened major opportunities to directly observe these levels [38–40].

2.3. Mulliken Difference Potential

We will also discuss the ‘Mulliken Difference Potential’ (MDP) in connection with radiative transition probabilities [41]. The MDP is basically the sum of the $R$-dependent local relative kinetic energy, $T_f(R)$, of the two nuclei in the initial state plus the potential energy of the final state, $V_f(R)$, since the nuclear kinetic energy is nearly unchanged during a nearly instantaneous electronic transition:

$$\text{MDP}(R) = T_f(R) + V_f(R)$$  \hspace{1cm} (2)

The transition probability will ordinarily be concentrated where the motion of the nuclei is slow, e.g. at the classical turning points. For a bound-bound transition involving two regular potentials, there are only four turning points to consider, but the situation quickly becomes more complex as the number of turning points increases. Obviously when an initial and a final turning point overlap, particularly strong transitions occur [18]. For long-range molecular levels near dissociation, the outer turning point strongly dominates. Moreover, when the MDP has an extremum, there is a build-up in probability in a narrow frequency region, first noted as ‘satellite bands’ (often free $\rightarrow$ free) in the neighborhood of atomic resonance lines [42]. These criteria for strong probability essentially provide the envelope of the results that can be more precisely calculated using Franck-Condon factors ($\langle e', v', J'|e'', v'', J'' \rangle \chi$) between the upper $e'$ PEC and the lower $e''$ PEC or, better yet, the square of the electronic dipole transition moment (EDTM) matrix element between the upper and lower level wavefunctions.

It should also be noted that nearly degenerate levels of two or more different electronic states frequently mutually perturb (mix with, couple to) each other. One of the first examples of perturbations was observed in Na$_2$ by R. W. Wood and co-workers in a series of 26 papers over 17 years (see [18] for discussion and a list). Magnetic rotation spectra were observed in the $A$ singlet state, which were subsequently established to be the result of the mixing of the $b$ triplet state with the $A$ state. The perturbations between these two states in Rb$_2$, KRb, and the other alkali metal diatomics are pervasive. There are a variety of selection rules for perturbations, e.g. the mutually perturbing rovibronic states must have the same total angular
momentum [1,2], but we will not enumerate them here. The perturbations are generally stronger when $\Delta \Omega = 0$ (homogeneous) and weaker when $\Delta \Omega = \pm 1$ (heterogeneous) [1]. In the case of ultracold molecules, the rotational quantum number $J$ is small (typically $J < 6$). Since nominally homogeneous perturbations are $J$ independent while heterogeneous perturbations are linear in $J$ [1], the ratio of homogeneous to heterogeneous perturbations is particularly large in the ultracold regime discussed in Section 4. Several other cases of mutually perturbing states are discussed below.

3. Radiative transition probabilities and selection rules

3.1. Radiative transition probabilities

The rovibronic transitions between two rovibrational levels in two different electronic states have been extensively studied in the alkali metal diatomics, at high (heat pipe oven), cold (supersonic molecular beam) and ultracold (magneto-optical or other traps) temperatures. For bound $\rightarrow$ bound transitions, the radiative transition probabilities (RTP) for both absorption and emission depend on the $R$-dependent part of the electronic dipole transition moment (EDTM), $d_{\text{if}} (R)$, between electronic states $i$ and $f$. This function is then evaluated between the radial part of the initial state rovibrational wavefunction, $|i, v_i, J_i\rangle$, in PEC$(i)$, and the radial part of the final state rovibrational wavefunction, $|f, v_f, J_f\rangle$, in PEC$(f)$, and then squared:

$$\text{RTP}(i \rightarrow f) \propto |\langle i, v_i, J_i | d_{\text{if}}(R) | f, v_f, J_f \rangle|^2$$

(3)

For bound $\rightarrow$ free (photodissociation) and free $\rightarrow$ bound (photoassociation) transitions, a continuum wavefunction must be used corresponding to wavefunction $k_f$ or $k_i$, respectively.

3.2. Electronic dipole transition moment (EDTM)

Since $d_{\text{if}}$ is a vector, the angular parts of the rovibrational matrix elements are nonzero only if $\Delta J = 0$ or $\pm 1$. Moreover, the electronic quantities $d_{\text{if}}$ are identically zero by symmetry for both homonuclear ($D_{\infty h}$) and heteronuclear ($C_{\infty v}$) diatomic molecules unless $\Delta \Lambda = 0$, $\pm 1$, $\Delta \Omega = 0$, $\pm 1$, and $\Delta S = 0$. Moreover, since the dipole moment is an odd operator with respect to inversion, only $g \rightarrow u$ and $u \rightarrow g$ transitions are nonzero for homonuclear molecules. Finally, for $\Sigma$ states, only $\Sigma^+ \rightarrow \Sigma^+$ and $\Sigma^- \rightarrow \Sigma^-$ transitions are nonzero. It should also be noted that $S$ and $\Lambda$ are not always good quantum numbers at long range and thus the short-range electronic state designations (Hund’s case a/b) should not always be used at long range in examining the implications of selection rules.

3.3. Nuclear spin state

A final consideration for the homonuclear diatomics is the nuclear spin state. For the bosonic nuclei of the alkalis, there are essentially two unaffiliated molecules: para, with even nuclear spin $I = 0, 2, 4$, etc. for even $J$, and ortho, with odd nuclear spin $I = 1, 3, 5$, etc. with odd $J$. For fermionic nuclei, the even nuclear spin states are connected with odd $J$, while the odd nuclear spin states are connected with even $J$. There are no allowed transitions between ortho and para states assuming the nuclear spin state is unchanged.

3.4. Probability criteria

The turning point ranges of the initial and final rovibrational states must overlap for significant transition probability. Moreover, the magnitude of the electronic dipole transition moment will normally be largest if there is a dipole-allowed and spin-allowed change in a single molecular orbital. For example in the homonuclear alkali-metal diatomics, the $A \leftarrow X$ and $A \rightarrow X$ transitions both correspond to changing between a $\sigma_g^2$ molecular orbital configuration and a $\sigma_g\sigma_u$ configuration. Likewise the $B \leftarrow X$ and $B \rightarrow X$ both correspond to changing between a $\sigma^2$ and a $\sigma_u\pi_u$ configuration. Both transitions are strong, essentially sharing the very strong atomic $ns \rightarrow np$ dipole transition moment, where $n = 2–6$ for Li to Cs. On the other hand, an excited state near a $nd$ atomic asymptote or a doubly excited asymptote may have a very weak electronic transition dipole moment to/from the $X$ state.

4. Types of cold and ultracold radiative transitions

Here we briefly examine the radiative transitions of cold and ultracold molecules, including molecular beam excitation spectra, laser-induced fluorescence spectra, ultracold photoassociative spectra, spontaneous emission of photoassociatively formed molecules, ultracold molecule excitation spectra, stimulated Raman transfer spectra, and multiple resonance spectra.

4.1. Molecular beam excitation spectra

A supersonic molecular beam (MB) of atoms often includes the corresponding diatomic, triatomic, and
other molecular species dependent on expansion conditions. The first work on this topic for alkali metals was in 1967 [43], which was followed by velocity distribution and magnetic deflection characterization in the Herschbach group [44] and then spectroscopic characterization [45,46]. In Li2, an oven temperature of 1370 K yielded a beam with a diatomic mole fraction of 10%, a TVib = 195 K, and a Trot = 70 K [46]. In the intervening decades, the conditions have been greatly improved, so that now [47,48], with (for KRb) TVib = 1 K (so that 95% of the vibrational population is in ν′ = 0) and Trot = 1.49 K (so one of the few most highly populated rotational levels is J″ = 0). Similar cold molecules can also be studied in a weakly interacting environment by matrix isolation spectroscopy and by spectroscopy of molecules in or on the surface of large He clusters, but we will not examine those options here.

The excitation spectra of such cold molecules are readily predicted using the PECs previously introduced. The spectra for Rb2 are readily predicted using a vertical line from the minimum of the X state as shown in Figure 7. Note that many of the excited electronic states cannot be accessed because of the strong singlet-triplet mixing. Two of the transitions are to the well known singlet states, the A and the B states. The other two states are the b state, which is known to be perturbed by the A state, and the 2 3Σ+ state, which may be weakly perturbed by singlet states, but has never been directly observed as it is purely repulsive with only continuum levels.

Because of the small range of vibration of the X state, only a small range of vibrational or continuum levels will be excited in each case. For the A state, the strongest excitation will be near 11,400 cm⁻¹ while that for the B will be near 14,600 cm⁻¹. All the absorption to the singlet states will be bound-bound. Absorption to the b state near 9700 cm⁻¹ is particularly interesting in that the absorption is nearly diagonal in v, i.e. the largest Franck-Condon factor for absorption is the v′ = 0 ← v′ = 0 band. However, the EDTM will be small since the region of the b state minimum is farthest below the A state minimum (where the singlet-triplet mixing would be stronger). Again only bound-bound transitions for low values of the upper vibrational quantum number ν′ are expected. The least certain excitation spectra are the bound → free spectra near 20,300 cm⁻¹, where a relative kinetic energy release of ~2900 cm⁻¹ between the two atoms is expected. The largest uncertainty is the magnitude of the EDTM between the two electronic states, which is expected to be quite small since little mixing with singlet states is expected for this triplet state. Nevertheless, photofragmentation of Rb2 near 20,300 cm⁻¹ to look for Rb2 loss or 5P3/2 production might be detectable.

For KRb, as shown in Figure 8, the situation is more complex. Since there is no longer u-g symmetry, all eight states at the K(4P)+Rb(5S) and the K(4S)+Rb(5P) limits now correspond to allowed transitions for at least some Ω components. In addition, the a → X photodissociative transition near 5500 cm⁻¹ is conceivable but probably quite weak (mixing of the a and b triplet states, the b state having already mixed with the A singlet state). There are four singlet and four triplet transitions to the two excited asymptotes at roughly 9600 (b), 11,300 (A), 14,500 (2 3Σ+), 15,000 (B), 15,100 (3 1Σ+), 16,900 (2 1Π), 17,900 (2 3Π), and 18,600 cm⁻¹ (3 3Σ+). Supersonic molecular beam experiments in the 14,890–15,850 cm⁻¹ range show each of the predicted states, which do mutually perturb each other, especially the 0+ component of the b and A states and the 1 components of the 1 1Π, 2 3Σ+, and b states [47,48]. The lowest five of these eight states yield only bound → bound absorption. The absorption to the 2 1Π state would also seem to be bound → bound; however, because the B and 2 1Π states are strongly mixed [49–51], levels above the
K(4S) + Rb(5P) limit also can predissociate. It is also worth noting that [51] shows the Franck–Condon factors for absorption to the 2 1 1Π and 1 3Σ states from \( v_0 = 0 \) of the \( \chi \) state as a function of the inner turning points \( R_{v'p} \) of the upper \( v' \) vibrational levels. For the first level of the 2 1 1Π state above the dissociation limit and low \( J' \), the fragment atoms will be quite cold translationally. The final two states (2 3Π and 3 3Σ) have been seen in ultracold molecule (UM) excitation spectroscopy [27] and the uppermost state (3 3Σ) has been seen in MB excitation spectroscopy, again where it is expected [52]. In these two states, all levels reached are either quasibound (and thus can predissociate by tunneling) or continuum. For the uppermost state, the MB spectra [52] included levels \( v' = 1–8 \) in the range 18,660.3–19,096.6 cm\(^{-1}\), whereas in the UM spectra [27] included levels \( v' = 4–12 \). Thus we expect that the MB experiments will yield only long-lived quasibound levels with negligible tunneling, since even the \( v' = 12 \) level shows no lifetime broadening. For the 2 3Π state, we believe direct photodissociation is more likely, since quasibound levels in the range 17,351.6–17,617.3 cm\(^{-1}\) were observed and the highest quasibound level predicted was at 17,659.1 cm\(^{-1}\), well below the 17,900 cm\(^{-1}\) centre frequency of the absorption estimated above. This photodissociation might well be interesting to study since the 5(0) component of the 2 3Π state correlates adiabatically to the K(4P) + Rb(5S) asymptote, but diabatically to the K(4P) + Rb(5S) asymptote, while the 6(1) component correlates both adiabatically and diabatically to the K(4P) + Rb(5S) asymptote.

4.2. Spontaneous emission of laser-excited rovibronic levels

The spontaneous emission of individual rovibronic levels of alkali metal diatomics following laser excitation is well known, both in molecular beam and in heat-pipe oven studies. A single example is shown in Figure 9 for Rb\(_2\) to clearly elucidate the use of the Mulliken Difference Potential to predict the emission. A fairly high level of the \( \chi \) state has been produced in some way; how will it decay by spontaneous emission? First we note the range of initial classical vibrational motion from an inner turning point of 6.5 \( \alpha_0 \) to an outer turning point of 16.3 \( \alpha_0 \). The corresponding local kinetic energy is 0 cm\(^{-1}\) at both turning points and reaches a maximum of 4200 cm\(^{-1}\) at the minimum of the \( \chi \) state PEC. We then add that to the final potential (the \( \lambda \) state) to obtain the MDP(R) shown in Figure 9. Note that this function increases from \( R_{v''} \) to a maximum near 11.3 \( \alpha_0 \) and then decreases smoothly to near dissociation at \( R_{v''} \). The portion of the MDP below the dissociation limit represents bound → bound spontaneous emission, which is particularly strong at the two turning points in the upper \( \chi \) state, which correspond to the inner turning point of the \( v' \) level...
and the outer turning point of the \( \nu_2 \) level of the \( X \) state. There is negligible emission to \( X \) state levels below \( \nu_1 \). A good example of such behavior is the corresponding transition in Na\(_2\) where the \( \nu_1 = 3 \) level of the \( X \) state is laser-excited to the \( \nu_1 = 34 \) level of the \( A \) state. The \( \nu_1 = 34 \) level then emits to levels \( \nu_1 = 3–56 \), the strongest emission by nearly a factor of three being to the \( \nu_1 = 43 \) level, which has virtually the same outer turning point as the \( \nu_1 = 34 \) level [18]. The level \( \nu_1 = 56 \) is the highest level in the EPEC for the \( J \) values involved in the transitions. Moreover, the emission to \( \nu_1 = 0–2 \) is negligible, as expected. The portion of the MDP above the dissociation limit represents bound \( \rightarrow \) free emission, where two free atoms fly apart with a relative kinetic energy corresponding to the energy above the dissociation limit. Moreover, there are two branches of the MDP (inside and outside the energy above the dissociation limit. Moreover, apart with a relative kinetic energy corresponding to bound \( \rightarrow \) continuum state with a kinetic energy of 1 mK corresponding to traditional photoassociation at high temperatures (\( T \leq 1 \) mK) [38–40] is completely different from traditional photoassociation at high temperature in the same spectral region [53]. Because an initial continuum state with a kinetic energy of 1 mK corresponds to an energy of 0.0007 cm\(^{-1}\), the free \( \rightarrow \) bound absorption spectra to excited rovibrionic levels near excited asymptotes appear as individual lines rather than a continuum (such as is seen at high temperatures), with a corresponding great increase in information content.

The usual result of PA is to form excited rovibrionic levels at long range, e.g. near the \( nS + nP \) asymptotes for the two colliding alkali atoms, either identical or different. Such a PA event is shown for KRb at the right-hand side of Figure 10. As shown in Figure 4, there are four asymptotes of increasing energy with three attractive states (\( 2(0^+), 2(0^-) \), and \( 2(1) \)), five attractive states (\( 3(0^+), 3(0^-), 3(1), 4(1), \) and \( 1(2) \)), three repulsive states (\( 4(0^+), 4(0^-), \) and \( 5(1) \)), and five repulsive states (\( 6(1), 2(2), 5(0^+), 5(0^-), \) and \( 7(1) \)), respectively. Long-range PA only occurs to the bound rovibrational levels of the attractive states, not to the continuum levels of the repulsive states at the excited

4.3. Photoassociation of ultracold atoms

The photoassociation (PA) of atoms at ultracold temperatures (\( T < 1 \) mK) [38–40] is completely different from traditional photoassociation at high temperature in the same spectral region [53]. Because an initial continuum state with a kinetic energy of 1 mK corresponds to an energy of 0.0007 cm\(^{-1}\), the free \( \rightarrow \) bound absorption spectra to excited rovibrionic levels near excited asymptotes appear as individual lines rather than a continuum (such as is seen at high temperatures), with a corresponding great increase in information content.

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![Figure 10. Photoassociation (PA) and spontaneous emission (SE) via a resonantly coupled level in KRb.](image)

K asymptotes. All eight attractive states were observed in our initial work on KRb [25,54].

At intermediate distances (Figure 6), PA should also occur to quasibound levels in the outer well of the \( 5(0^+) \) state near \( 18 \) \( \alpha_0 \) and then to further quasibound levels in the \( 2 \) \( ^3\Pi \) and \( 3 \) \( ^3\Sigma^+ \) states near \( 11\alpha_0 \). These quasibound levels have been observed by ultracold molecule (UM) spectroscopy, but not yet by PA [27].

In Rb\(_2\), as shown in Figure 3, there are four asymptotically attractive states (\( 1(0^+g), 1(1g), 1(0^+_u), \) and \( 2(0^-_u) \)) and two asymptotically repulsive states (\( 2(1_u) \) and \( 2(0^+_g) \)) at the Rb(5S)+Rb(5P\(_3/2\)) limit. PA to the four attractive states occurs as expected. For the initially repulsive \( 2(1_u) \) state, there is a maximum at \( 34 \alpha_0 \), and attraction inside, so PA to quasibound and then bound levels is possible. Electronic predissociation of the bound levels of the \( 2(1_u) \) state (correlating to the Rb(5S)+Rb(5P\(_3/2\)) asymptote) by the purely repulsive \( 2(0^+_g) \) state was observed in K\(_2\) by observation of the K(4P\(_1/2\)) fragments [55].

For the Rb(5S)+Rb(5P\(_3/2\)) asymptote, there are five asymptotically attractive states (\( 2(0^+_g), 2(1_g), 1(2_u), 2(0^-_g), \) and \( 3(1_u) \)) and five asymptotically repulsive states (\( 3(1_g), 1(2_g), 3(0^-_g), 3(1_u), \) and \( 3(0^+_g) \)). The two least attractive of the five attractive states become repulsive at intermediate range as \( R \) decreases and are known as ‘pure long range molecules’ since their entire potential energy well can be simply and analytically described using the properties of separated atoms [20,36]. PA to most of the asymptotically attractive states has been observed.

An unusual type of Rb\(_2\) PA, ‘blue-detuned PA’ to quasibound levels, is shown in Figure 11. Here the relatively small amplitude of the wavefunction for two
colliding ground state atoms at the intermediate-range inner turning point of the $a$ state allows us to reach the well of the $^1 \Sigma_\text{g}$ state, which contains quasibound levels for all four $^1 \Sigma_\text{g}$ components ($3(0 g)$, $2(0 g)$, $3(1 g)$, and $1(2 g)$). The $3(0 g)$ component has a second outer well near $18 \alpha_0$. We have observed the levels of all five wells [26].

4.4. Spontaneous emission of PA-formed molecules

For the vast majority of PA experiments, the spontaneous emission of PA-formed molecules is very simple: PA forms an excited long-range molecule, which emits preferentially to form a long-range molecule in the $X$ or $a$ state near their dissociation limit of two ground state atoms or to re-form a pair of ground state atoms in the continuum. In other words the MDP strongly favors emission in the region very near the dissociation limit. For example, our work on KRb identified levels $v'' = 86-92$ of the $X$ state and $v'' = 17-23$ of the $a$ state, all within $30 \text{cm}^{-1}$ of the dissociation limit [56]. The numbering up to $v'' = 87$ of the $X$ state was previously established [57] and the numbering up to $v'' = 25$ of the $a$ state has now been seen [15].

However, as we will examine in detail below, there are often other levels we would like to reach, so-called ‘target levels’, for a variety of reasons. For example, the lowest rovibrational level of the $X$ state, $X(0, 0)$ for short, will not experience inelastic collisions (except for excited hyperfine states) at ultracold temperatures and, for heteronuclear molecules, will have the largest dipole moment; it will also have a simple and sparse excitation spectrum, similar to that of a molecular beam as described in Figures 7 and 8 above.

An example of a method to reach $X(0, 0)$ more directly is the use of resonant coupling of excited states, shown on the left-hand side of Figure 10 for KRb [51]. As is obvious in Figure 2, the PECs of the $B$ and $2^1 \Pi$ states undergo an avoided crossing and consequently nearly degenerate levels in the two PECs mutually perturb each other and are strongly mixed in character. The $B^1 \Pi$ portion of the mixed wavefunction provides the long-range PA probability while the $2^1 \Pi$ portion provides good overlap with the $X(0, 0)$ level; at the same time the $2^1 \Pi$ portion has virtually no long-range PA probability (it is a repulsive PEC at long range) and the $B^1 \Pi$ portion has very small overlap with the $X(0, 0)$ level. Preliminary observations of the KRb mixed levels ($B^1 \Pi (v'' = 60)$ and $2^1 \Pi (v'' = 17)$) have been published, along with predictions of resonant coupling in the other heteronuclear alkali diatomics [51].

Feshbach resonances have a long and interesting history [58]. For molecules, they occur whenever a nominally bound state of a given PEC is embedded in and coupled to the continuum of another PEC; in other words, it corresponds to an electronic predissociation. However, rather than observing the fragmentation of a molecule into atoms, one has a scattering resonance which should appear in the collision cross section between two atoms at a fixed resonance energy with a fixed width. For ultracold science, however, it is not the fixed energy resonances which are of interest; it is the tunable resonances at near zero energy near threshold [58]. While electric and optical fields can also be used, it is the magnetically tunable Feshbach resonances which have been most studied. Such resonances have been tuned with a magnetic field across threshold to convert two colliding atoms by magnetodissociation (MA) into a bound molecule in a level exceedingly close to the dissociation limit (a so-called Feshbach molecule); the reverse process of magnetodissociation works equally well in many cases. In recent years there have been two related proposals to combine PA with MA [59,60] in so-called Feshbach-Optimized PhotoAssociation (FOPA) to couple the $X$ and $a$ states extremely close to the dissociation limit to greatly enhance the scattering.

Figure 11. Photoassociation (PA), spontaneous emission (SE), and resonant two-photon ionization (R2PI) in Rb$_2$ from Figure 1 and [14] and in Rb$_2^+$ from [69].
wavefunction at short internuclear distances and enhance PA rates by many orders of magnitude compared to field-free PA.

Yet another approach is to use intermediate-range PA such as that shown in Figure 11. Indeed that has been shown to efficiently produce the lowest level of the \( a \) state, \( a(0,0) \) [26].

Two-photon PA to reach Rydberg states, as originally suggested by Band and Julienne [61], was first used to produce spontaneous emission to the \( X (v = 0) \) vibrational level in several low \( J \) rotational levels in the case of \( K_2 \) [62].

Finally, the use of stimulated Raman transfer, suggested by Bahns, Gould and Stwalley [63], has been successfully carried out for KRb [64,65], as discussed in Section 4.6 below.

4.5. State-selective excitation/detection of ultracold molecules near dissociation

With the high sensitivity of techniques such as time-of-flight mass spectroscopic detection, it is possible to not only photoassociate ultracold atoms to form excited ultracold molecules which decay to form \( X \) and \( a \) state ultracold molecules; but also it is feasible to observe the spectra of small samples of these ultracold molecules. Such UM spectra were initially based on the resonances in resonance-enhanced multiphoton ionization (REMPI) state-selective detection with pulsed lasers [56,66,67]. Subsequently higher resolution was achieved by depletion of the REMPI signals with cw lasers [68].

Resonance-enhanced two photon ionization (R2PI) detection of the \( a \) state vibrational levels of \( Rb_2 \) is conveniently carried out through the \( 2 \, ^3 \Pi_g \) state and other nearby states, as illustrated in Figure 11 and described in [67]. For the \( X \) state, the \( 2 \, ^1 \Sigma_u^+ \) state is similarly convenient [66].

For KRb, as shown in Figure 12, detection through the \( 4 \, ^1 \Sigma^+ \) state works well for the \( X \) state while detection through the \( 4 \, ^3 \Sigma^+ \) state works well for the \( a \) state [56,71].

4.6. Stimulated Raman transfer of ultracold molecules

Currently there have only been two successful experiments (for any molecules) to exclusively produce the \( X(0,0) \) target levels; both have been for KRb and both involve stimulated Raman transfer (SRT) [64,65]. The former experiment [64] involved starting in a very high level of the \( a \) state (formed by magnetoassociation through a Feshbach resonance [58,72]). This level was then transferred with over 90% efficiency through a mixed singlet-triplet level to the \( X(0,0) \) level by stimulated Raman transfer. The latter experiment [65] used PA to form high levels of the \( X \) state. The population of a single one of these levels was then transferred by SRT through an intermediate singlet level in the \( 3 \, ^1 \Sigma^+ \) state to \( X(0,0) \) [65], as was earlier proposed [68].

Recently we have shown, using KRb as an example, how to experimentally determine the optimal path for SRT from a high \( X \) or \( a \) state level to \( X(0,0) \) in heteronuclear alkali diatomics [47,48]. Promising paths for the singlet→singlet and triplet→singlet SRT in KRb are shown in Figures 13 and 14, respectively. At ultracold temperatures, the small rotational splittings are unresolved. Determination of the optimal path is particularly important for the triplet→singlet transfer case in Figure 14 since the best intermediate levels are strongly perturbed levels. They must have both a large singlet and a large triplet component so that the initial excitation (PUMP) from
the triplet will be efficient and the final de-excitation (DUMP) to the singlet will also be efficient. The key in finding optimal paths is first to shift the energy axes of the spectra so that they are plotted versus the energy of the upper intermediate levels for both the molecular beam (MB) and the ultracold molecule (UM) excitation spectra. Then for a specific initial lower level (e.g. the $v'' = 21$ level of the $a$ state), the product of the MB and the UM spectra (MBxUM) will show directly the optimal paths from $a (v'' = 21, J'')$ to $X (0, 0)$. For the example shown in the MBxUM product spectrum in Figure 2 in [48], the intermediate levels showing the four strongest peaks are labeled $\alpha, \beta, \gamma$, and $\delta$, where $\gamma$ is the strongest and $\beta$ the second strongest. We know now that these strongest peaks correspond to levels $v' = 8$ and 7 of the $B ^1\Pi$ state, respectively, each of which is strongly mixed with (perturbed by) a different unknown triplet vibrational level. The two unknown triplet vibrational levels in turn represent peaks $\alpha$ and $\delta$, respectively, each of which is strongly mixed with the nearby singlet level, $v' = 7$ and 8 of the $B$ state, respectively. However, note that it is not necessary to assign the highly perturbed spectra in order to implement the optimal path, since the two frequencies for the SRT are already determined.

4.7. Multiple resonance spectroscopy of ultracold molecules

There are a number of additional directions for UM spectroscopy we have not yet mentioned here. One promising direction is the observation of potential curves at very large internuclear distances, such as we studied in K$_2$ [73]. By exciting first the pure long range molecular levels of the $2(0_{g})$ (or $3(1_u)$) states of K$_2$, resonant ionization through levels slightly below the 4D, 6S, 5D, 7S, and 6D was observed. For the first two atomic limits (4D and 6S), autoionization is energetically impossible and sharp spectra are observed, while for the higher limits, line broadening attributed to autoionization is observed. Two-color two-photon excitation of Rydberg states was used to produce $X(0, J')$ ultracold molecules [62].

Another interesting approach is to try to reach unusual states [38]. For example the outer well of the $3 ^1\Pi_g$ state of Na$_2$ could potentially be reached in four steps starting in low levels of the $X$ state, while only two steps would be required starting with PA. In a similar way, two steps could reach the high Rydberg levels of Na$_2$ and autoionization resonances, whereas three steps were required starting from low levels of the $X$ state. Studies of ion-pair ('heavy Rydberg') states also look promising.

4.8. Target levels

A variety of levels are interesting targets for experiments of various kinds in addition to the $X(0, 0)$ level discussed in Sections 4.4 and 4.6 above.

For homonuclear diatomics, para and ortho species exist separately and are not connected optically. If no collisions with paramagnetic species are involved,
studies with \( X(0, 1) \) (or \( (0, 1) \) levels of other electronic states) might be quite interesting because of their resultant metastability. Techniques for producing \( X(0, 1) \) may be even simpler than those for \( X(0, 0) \) since spontaneous emission from a \( J' = 0 \) level often produces only \( J' = 1 \).

The lowest level of the \( a \) state, \( a(0, 0) \), will certainly have a very long radiative lifetime and may well survive collisions with non-paramagnetic species. We have already established pathways for efficient production of \( a(0, J') \) using blue-detuned PA to the \( 1^3\Pi_g \) state of \( \text{Rb}_2 \) [26]; analogous intermediate levels have also been observed for the \( 2^3\Pi \) state of \( \text{KRb} \) [27].

The low levels of the \( b \) state in the homonuclear alkali diatomics may also be quite interesting. The interactions between the triplet \( b \) and the singlet \( A \) state are well known and large compilations of data have been impressively analyzed by Bergeman, Lyrra, and coworkers ([74,75,76,77] for \( \text{Na}_2 \), \( \text{K}_2 \), \( \text{Rb}_2 \), and \( \text{Cs}_2 \), respectively). The \( 0^+ \) component of the \( b \) state mixes strongly with that of the \( A \) state, resulting in a radiative lifetime of only \( 26 \mu s \) in \( \text{Cs}_2 \) [77]; the radiative lifetime should be similar in \( \text{Rb}_2 \). The radiative lifetimes of the \( 0^+, 1^-, \) and \( 2 \) components should be much longer. Moreover, the levels are closely spaced (especially the \( 0^+ \) and \( 0^- \) components) and are coupled in complex and variable ways by spin-orbit, collisions, and electromagnetic fields. The equilibrium internuclear distances and vibrational frequencies of the \( X \) and the \( b \) states are very similar and the corresponding Franck-Condon factors should be near diagonal, especially for low \( v \). This set of levels deserves further theoretical and experimental investigation.

Finally we note that accurate observations of the lowest levels of the lowest two electronic states of \( \text{Rb}_2^+ \) and \( \text{KRB}^+ \) are desirable, since both ionization potentials are uncertain by \( >100 \text{ cm}^{-1} \) [78]. The lower energy strongly bound ground state, \( \text{X}^2\Sigma^+ \) (which is gerade for \( \text{Rb}_2 \)) has properties such as \( R_e \) and \( \omega_b \) known from observations of Rydberg states. The second state, \( A^2\Sigma^+ \) (which is ungerade for \( \text{Rb}_2 \)) with an antibonding orbital occupied, is attractive at long range because of the charge-induced dipole \( R^{-4} \) attraction. As far as we can tell, the Rydberg states correlating with this second state at \( 18–20 \text{a}_u \) have not been observed. An additional reason for such study is to attempt to directly produce the \( (0, 0) \) level in each state by autoionization, as was previously observed in \( \text{Na}_2 \) [79].

5. Conclusions
This paper has presented a variety of shortcuts and insights, primarily graphical and semiclassical, for simply understanding the spectroscopy of ultracold molecules using the alkali diatomics and their PECs, especially \( \text{Rb}_2 \) and \( \text{KRB} \), for examples. It is hoped that these approaches will help to advance the impressive progress being made in this exciting field.

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